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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : <b>C01G 45/12, 45/02, H01M 4/50, B01J 23/32, A45D 20/40, A21B 2/00, H05B 3/10</b>	A1	(11) International Publication Number: <b>WO 00/27754</b> (43) International Publication Date: 18 May 2000 (18.05.00)
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(22) International Filing Date: 8 November 1999 (08.11.99)		(81) Designated States: CA, CN, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data: 09/188,770 9 November 1998 (09.11.98) US 09/188,768 9 November 1998 (09.11.98) US 09/203,414 2 December 1998 (02.12.98) US 09/334,203 16 June 1999 (16.06.99) US		Published <i>With international search report.</i>
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(54) Title: METAL OXIDE PARTICLES		
(57) Abstract		

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-1-

## METAL OXIDE PARTICLES

### FIELD OF THE INVENTION

The invention relates to metal oxide powders. More particularly, the invention relates to nanoscale 5 metal oxide particles, such as manganese oxide particles and lithium manganese oxide particles, produced by laser pyrolysis. The invention further relates to methods for producing metal oxide powders with laser pyrolysis and aerosol precursors. Furthermore, the invention relates 10 to methods of producing ternary particles, especially crystalline nanoparticles, by laser pyrolysis.

### BACKGROUND OF THE INVENTION

Advances in a variety of fields have created a demand for many types of new materials. In 15 particular, a variety of chemical powders can be used in many different processing contexts, such as the production of batteries. Specifically, there is considerable interest in the application of ultrafine or nanoscale powders that are particularly advantageous for 20 a variety of applications involving small structures or high surface area materials. This demand for ultrafine chemical powders has resulted in the development of sophisticated techniques, such as laser pyrolysis, for the production of these powders.

25 The microminiaturization of electronic components has created widespread growth in the use of portable electronic devices such as cellular phones, pagers, video cameras, facsimile machines, portable stereophonic equipment, personal organizers and personal 30 computers. The growing use of portable electronic equipment has created ever increasing demand for improved power sources for these devices. Relevant batteries include primary batteries, i.e., batteries

-2-

designed for use through a single charging cycle, and secondary batteries, i.e., batteries designed to be rechargeable. Some batteries designed essentially as primary batteries may be rechargeable to some extent.

5           Batteries based on lithium have been the subject of considerable development effort and are being sold commercially. Lithium based batteries generally use electrolytes containing lithium ions. The negative electrodes for these batteries can include lithium metal  
10          or alloy (lithium batteries), or compositions that intercalate lithium (lithium ion batteries). Preferred electroactive materials for incorporation into the positive electrodes are compositions that intercalate lithium. The compositions that intercalate lithium, for  
15          use in the positive electrodes, generally are chalcogenides such as metal oxides that can incorporate the lithium ions into their lattice.

Manganese can exist in various oxidation states. Correspondingly, manganese oxides are known to  
20          exist with various stoichiometries. In addition, manganese oxides with a particular stoichiometry can have various crystalline lattices, or they can be amorphous. Thus, manganese oxides exhibit an extraordinarily rich phase diagram.

25          Manganese oxides and lithium manganese oxides with various stoichiometries have been noted as promising materials for use in positive electrodes for lithium based batteries. In particular, appropriate manganese oxides can intercalate lithium ions into their  
30          crystal structure to form lithium manganese oxides. Lithium manganese oxides are useful for the production of lithium based secondary batteries. Because of the interest in lithium manganese oxides, several approaches

-3-

have been developed for producing lithium manganese oxide powders.

SUMMARY OF THE INVENTION

In a first aspect, the invention pertains to  
5 a collection of particles comprising manganese oxide, the collection of particles having an average diameter less than about 500 nm, the manganese oxide having a structure selected from the group consisting of amorphous manganese oxide, crystalline MnO, crystalline  
10 Mn<sub>5</sub>O<sub>8</sub> and crystalline Mn<sub>2</sub>O<sub>3</sub>.

In another aspect, the invention pertains to a method of producing a metal oxide powder, the method comprising reacting an aerosol within a reaction chamber to form metal oxide particles, the aerosol comprising a metal precursor and the metal oxide particles having an  
15 average diameter less than about 500 nm.

In a further aspect, the invention pertains to a method for altering the stoichiometry of a collection of manganese oxide particles, the method comprising heating manganese oxide particles in an oxidizing environment at a temperature less than about 600°C.  
20

In another aspect, the invention pertains to a battery having a cathode comprising manganese oxide particles, said manganese oxide particles having an  
25 average diameter less than about 250 nm.

In addition, the invention pertains to a method of producing a composite metal oxide particles, the method comprising reacting an aerosol to form a powder of composite metal oxide particles with an average diameter less than about one micron, the aerosol comprising a first metal compound precursor and a second metal compound precursor.  
30

In a further aspect, the invention pertains to a method for producing lithium metal oxide, the method

-4-

comprising pyrolyzing a reactant stream in a reaction chamber, the reactant stream comprising a lithium precursor, a non-lithium metal precursor, an oxidizing agent, and an infrared absorber, where the pyrolysis is  
5 driven by heat absorbed from a light beam.

In another aspect, the invention pertains to a collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, wherein the collection  
10 of particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

15 Furthermore, the invention pertains to a method of making lithium manganese oxide particles comprising heating a mixture of manganese monoxide (MnO) particles and a lithium compound, the manganese monoxide particles having an average diameter less than about 250  
20 nm.

Moreover, the invention pertains to a method of making lithium manganese oxide particles comprising heating a mixture of particles of a manganese oxide and a lithium compound, the particles of manganese oxide  
25 having an average diameter less than about 250 nm, wherein the resulting lithium manganese oxide particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.  
30

In a further aspect, the invention features a battery comprising lithium manganese oxide particles having an average diameter less than about 250 nm, wherein the lithium manganese oxide particles have a

-5-

distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

5        In another aspect, the invention features a battery comprising lithium manganese oxide, the battery having a four volt profile with a cycling stability within about 20 percent of initial values after 25 cycles.

10      In addition, the invention features a battery comprising lithium manganese oxide, the battery having an initial capacity greater than 120 mAh\g.

15      Moreover, the invention pertains to a collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, the lithium manganese oxide comprising  $\text{Li}_2\text{Mn}_4\text{O}_9$ .

20      In a further aspect, the invention pertains to a collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, the lithium manganese oxide having a lattice parameter along axis a of no more than 8.23 angstroms.

25      Furthermore, the invention pertains to a method of producing crystalline ternary particles comprising reacting a reactant stream comprising precursors including the three atoms of the product ternary particles, wherein the relative amounts of the 30 three atoms in the reactant stream and the reaction conditions are selected to yield the crystalline ternary particles.

In another aspect, the invention pertains to a method of producing crystalline lithium manganese

-6-

oxide particles comprising reacting a reactant stream comprising a manganese precursor and a lithium precursor, wherein the reaction is driven by energy from electromagnetic radiation.

5        In a further aspect, the invention pertains to a collection of particles comprising a crystalline multiple metal oxide having an average particle diameter less than about 500 nm, wherein the lithium manganese oxide particles have a distribution of particle sizes in  
10      which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

BRIEF DESCRIPTION OF THE DRAWINGS

15      Fig. 1 is a schematic sectional view of a solid precursor delivery system taken through the center of the system.

20      Fig. 2 is a schematic, sectional view of an embodiment of a laser pyrolysis apparatus, where the cross section is taken through the middle of the laser radiation path. The upper insert is a bottom view of the collection nozzle, and the lower insert is a top view of the injection nozzle.

25      Fig. 3 is a schematic, side view of a reactant delivery apparatus for the delivery of vapor reactants to the laser pyrolysis apparatus of Fig. 2.

30      Fig. 4A is a schematic, side view of a reactant delivery apparatus for the delivery of an aerosol reactant to the laser pyrolysis apparatus of Fig. 2.

Fig. 4B is a schematic, side view of an alternative embodiment of a reactant delivery apparatus for the delivery of an aerosol reactant to the laser pyrolysis apparatus of Fig. 2.

- 7 -

Fig. 4C is a schematic, side view of another alternative embodiment of a reactant delivery apparatus for the delivery of an aerosol reactant to the laser pyrolysis apparatus of Fig. 2.

5 Fig. 5 is a schematic, perspective view of an elongated reaction chamber for the performance of laser pyrolysis, where components of the reaction chamber are shown as transparent to reveal internal structure.

10 Fig. 6 is a perspective view of an embodiment of an elongated reaction chamber for performing laser pyrolysis.

Fig. 7 is a cut away, side view of the reaction chamber of Fig. 6.

15 Fig. 8 is a partially sectional, front view of the reaction chamber of Fig. 6, taken along line 8-8 of Fig. 6.

20 Fig. 9 is a sectional, front view of a reactant delivery apparatus for the delivery of an aerosol reactant into the reaction chamber of Fig. 6, where the cross section is taken through the center of the reactant delivery apparatus.

Fig. 10 is a fragmentary, sectional front view of the top portion of the reactant delivery apparatus of Fig. 9.

25 Fig. 11 is a top view of the mount of the reactant delivery apparatus of Fig. 9.

Fig. 12 is a top view of a cap of the aerosol delivery apparatus of Fig. 9.

30 Fig. 13 is a sectional view of the cap of Fig. 12 taken along line 13-13.

Fig. 14 is a sectional side view of a spacer used in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the spacer.

-8-

Fig. 15 is a sectional side view of a shim used in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the shim.

5 Fig. 16 is a sectional, side view of an embodiment of a brushing cap for use in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the brushing cap.

10 Fig. 17 is a sectional, side view of an alternative embodiment of a brushing cap for use in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the brushing cap.

15 Fig. 18 is a sectional, side view of a second alternative embodiment of a brushing cap for use in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the brushing cap.

Fig. 19 is a side view of an ultrasonic aerosol generator having an atomization surface.

20 Fig. 20 is a sectional, side view of the ultrasonic aerosol generator of Fig. 19, where the cross section is taken through the center of the apparatus.

Fig. 21 is a schematic, side view of a liquid supply system for supplying liquid to the aerosol generator of Figs. 19 and 20.

25 Fig. 22A is a schematic, sectional view of an apparatus for heat treating nanoparticles, in which the section is taken through the center of the apparatus.

Fig. 22B is a schematic, sectional view of an oven for heating nanoparticles, in which the section is taken through the center of a quartz tube.

30 Fig. 23 is a schematic, perspective view of a battery of the invention.

Fig. 24 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with

- 9 -

gaseous reactants according to the parameters specified in column 1 of Table 1.

Fig. 25 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with 5 gaseous reactants according to the parameters specified in column 2 of Table 1.

Fig. 26 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with 10 gaseous reactants according to the parameters specified in column 3 of Table 1.

Fig. 27 is a transmission electron micrograph of manganese oxide nanoparticles produced by laser pyrolysis with gaseous reactants according to the parameters specified in column 2 of Table 1.

15 Fig. 28 is a plot of particle diameter distribution for the particles shown in the transmission electron micrograph shown in Fig. 27.

Fig. 29 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with an 20 aerosol manganese precursor according to the parameters specified in Table 2.

Fig. 30 is a transmission electron micrograph of manganese oxide nanoparticles produced by laser pyrolysis with an aerosol manganese precursor according 25 to the parameters specified in Table 2.

Fig. 31 is a plot of particle size distribution for the particles shown in the transmission electron micrograph of Fig. 30.

Fig. 32 is an x-ray diffractogram of manganese oxide nanoparticles following a heat treatment of 30 particles produced by laser pyrolysis, sample 1 of Table 3.

Fig. 33 is an x-ray diffractogram of manganese oxide nanoparticles following a heat treatment of

-10-

particles produced by laser pyrolysis, sample 2A of Table 3.

Fig. 34 is an x-ray diffractogram of manganese oxide nanoparticles following a heat treatment of 5 particles produced by laser pyrolysis, sample 2B of Table 3.

Fig. 35 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis using with aerosol reactants according to the parameters 10 specified in column 1 of Table 4.

Fig. 36 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis using with aerosol reactants according to the parameters specified in column 2 of Table 4.

15 Fig. 37 is an x-ray diffractogram of nanoparticles of lithium manganese oxide produced by laser pyrolysis of a reactant stream with an aerosol.

Fig. 38 is an x-ray diffractogram of 20 nanoparticles of lithium manganese oxide made by laser pyrolysis following heating in an oven.

Fig. 39 is a plot of three x-ray diffractograms for three samples of lithium manganese oxide produced by heat treating mixtures of nanocrystalline manganese oxide and lithium nitrate.

25 Fig. 40 is a transmission electron micrograph of manganese oxide nanoparticles used for further heating processing into lithium manganese oxide.

Fig. 41 is a transmission electron micrograph 30 of lithium manganese oxide nanoparticles from sample 1.

Fig. 42 is an x-ray diffractogram for a sample of lithium manganese oxide particles directly produced by laser pyrolysis.

-11-

Fig. 43 is a transmission electron micrograph of lithium manganese oxide particles corresponding to the x-ray diffractogram of Fig. 42.

5 Fig. 44 is a plot of two x-ray diffractograms of mixed phase materials including silver vanadium oxide nanoparticles produced directly by laser pyrolysis, where each plot is produced with materials produced under slightly different conditions.

10 Fig. 45A is a transmission electron micrograph of the materials from the sample corresponding to the upper diffractogram in Fig. 44.

Fig. 45B is a transmission electron micrograph of the materials from the sample corresponding to the lower diffractogram in Fig. 44.

15 Fig. 46 is a plot of particle size distribution for the particles shown in the transmission electron micrograph of Fig. 45.

Fig. 47 is a schematic, perspective view of the two electrode arrangement used in the examples.

20 Fig. 48 is a plot of cell voltage in a range of four volts for four different positive electrode active materials.

25 Fig. 49 is a plot of cell voltage in a range of three volts for four different positive electrode active materials.

Fig. 50 is a plot of capacity as a function of cycle number for eight different cells produced with four different positive electrode active materials.

30 Fig. 51 is a schematic, perspective view of the three electrode arrangement used for the following tests.

Fig. 52 is a plot of voltage as a function of specific capacity for two nanoscale samples and a commercial lithium manganese oxide.

-12-

Fig. 53 is a plot of differential capacity for the samples used in Fig. 52.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 Several approaches are described for the production of metal oxide nanoparticles. These approaches provide for the production of metal oxide particles, such as manganese oxide nanoparticles, with a wide range of properties. Aerosol based approaches  
10 are described that can make use of low cost precursors to produce nanoparticles with a high production rate. Preferred collections of metal oxide particles have an average diameter less than a micron and a very narrow distribution of particle diameters. Laser pyrolysis  
15 with or without additional processing is a versatile approach for the production of a wide range of manganese oxide materials. The aerosol based approaches described herein can be used in the production of many other metal oxide nanoparticles.

20 In particular, several alternative approaches for the formation of nanoscale, crystalline ternary particles have been discovered. Crystalline, ternary particles has three types of atoms located at particular lattice sites within a crystal structure. Ternary  
25 particles of lithium metal oxide, such as lithium manganese oxide, are of particular interest because of their usefulness in battery applications.

In a first approach, it has been discovered that nanoscale manganese oxides provide a suitable  
30 starting material for the formation of nanoscale lithium manganese oxides. In particular, lithium manganese oxides with an average diameter less than a micron can be formed with a spinel crystal structure by thermal processing approaches with nanoscale manganese oxide

-13-

starting materials. The use of a nanoscale starting material allows for the use of very mild temperatures in the processing. The resulting nanoscale lithium manganese oxide spinels provide an excellent material 5 for the formation of lithium based batteries.

Alternatively, lithium manganese oxide nanoparticles can be formed by laser pyrolysis. Amorphous lithium manganese oxide particles produced by laser pyrolysis can be heated under mild conditions to 10 anneal the particles producing a spinel crystal structure. Furthermore, it has been discovered that crystalline lithium manganese oxide nanoparticles can be produced directly by laser pyrolysis. The lithium manganese oxide powders produced by laser pyrolysis can 15 be subjected to a heat treatment to alter and/or improve the properties of the particles. Thus, alternative approaches have been found useful to produce lithium manganese oxide nanoparticles.

More specifically, in a first approach the 20 lithium manganese oxide particles are formed by heating a mixture of nanoscale manganese oxide particles and a lithium compound. During the heating step the lithium is incorporated into the manganese oxide lattice. The manganese oxide particles for thermal lithium 25 incorporation can have a variety of stoichiometries including, surprisingly, MnO. The heating can be performed either under an oxidizing atmosphere or under an inert atmosphere. Due to the nanoscale character of the manganese oxide starting material, the heating can 30 be performed under surprisingly mild conditions. Under these mild reaction conditions, lithium manganese oxide particles are formed that have an average diameter less than a micron.

-14-

A preferred approach for the formation of suitable nanoscale manganese oxide particles for lithiation involves laser pyrolysis. In particular, laser pyrolysis is an excellent process for efficiently 5 producing manganese oxide particles and other metal oxide particles with a narrow distribution of average particle diameters.

A basic feature of successful application of laser pyrolysis for the production of metal oxide 10 nanoparticles is the generation of a reactant stream containing a metal precursor compound, a radiation absorber and a secondary reactant. The secondary reactant can be an oxygen source. The reactant stream is pyrolyzed by an intense laser beam. As the reactant 15 stream leaves the laser beam, the particles are rapidly quenched.

To perform laser pyrolysis, reactants can be supplied in vapor form. Alternatively, one or more reactants can be supplied as an aerosol. The use of an 20 aerosol provides for the use of a wider range of metal precursors for laser pyrolysis than are suitable for vapor delivery only. Thus, less expensive precursors can be used with aerosol delivery. Suitable control of 25 the reaction conditions with the aerosol results in nanoscale particles with a narrow particle size distribution. The heat processing of manganese oxide nanoparticles to form lithium manganese oxide nanocrystals and batteries formed from these nanoparticles are described below.

As an alternative to producing lithium manganese oxide nanoparticles by the thermal processing 30 of manganese oxide particles, lithium manganese oxide particles having diameters substantially less than a micron have been produced directly by laser pyrolysis.

-15-

For the direct production of lithium/manganese composite materials, laser pyrolysis preferably involves an aerosol based reactant delivery apparatus. Heat processing of the composite particles results in 5 crystalline lithium manganese oxide particles with a spinel crystal structure. The formation of nanoscale, amorphous lithium manganese oxide directly by laser pyrolysis is described further below.

Laser pyrolysis experiments described below in 10 the examples result in the production of amorphous lithium manganese oxide nanoparticles. In other experiments, the parameters of the laser pyrolysis synthesis have been adjusted to yield crystalline lithium manganese oxide nanoparticles directly by laser 15 pyrolysis. These are also described below in the examples. The phase diagram of the materials to be produce can guide the selection of appropriate laser pyrolysis conditions. In addition, the parameters can be adjusted empirically to arrive at suitable conditions 20 for the production of desired crystalline ternary particles. In particular, for the production of spinel  $\text{LiMn}_2\text{O}_4$ , production is favored by high chamber pressures, high flow rates of oxygen, low laser intensity for water based aerosols, and relatively 25 higher laser intensity for aerosols based on water and isopropyl alcohol.

The production of a substituted metal oxide  $\text{Ti}_{1-x}\text{V}_x\text{O}_2$  by laser pyrolysis has been described by Musci et al., "Laser synthesis of vanadium-titanium oxide 30 catalysts," J. Mater. Res. Vol. 7(10): 2846-2852 (October 1992), incorporated herein by reference. In these substituted metal oxides, vanadium substitutes at a lattice site for a titanium atom. The value of x could only be increased up to about 0.25 before a

-16-

separate vanadium oxide phase formed. These substituted metal oxides are not crystalline ternary compounds since the metal atoms are not at unique lattice sites. In crystalline ternary compounds, each atom is located at 5 a particular lattice site to yield a particular crystal structure. Similar substitution compounds with titanium substituting for chromium in Cr<sub>2</sub>O<sub>3</sub> were described by Schramm et al., U.S. Patent 5,013,706, "Metal Oxide Powders Or Their Mixtures And Their Use In Catalytic Dehydrogenation Of Hydrocarbons," incorporated herein by 10 reference.

As noted above, various forms of manganese oxides and lithium manganese oxides can reversibly intercalate lithium atoms and/or ions. The manganese oxide and/or lithium manganese oxide nanoparticles can 15 be incorporated into a positive electrode film with a binder such as a polymer. The film preferably includes additional electrically conductive particles held by the binder along with the lithium manganese oxide particles. 20 The positive electrode film can be used in a lithium battery or a lithium ion battery. The electrolyte for lithium and lithium ion batteries comprises lithium ions.

A. Particle Production Using Laser Pyrolysis

Laser pyrolysis has been discovered to be a valuable tool for the production of nanoscale metal oxide particles, in particular manganese oxide particles for further processing into lithium manganese oxide or 25 for the direct production of lithium manganese oxide particles. In addition, the particles produced by laser pyrolysis are a convenient material for further processing to expand the pathways for the production of desirable metal oxide particles. Thus, using laser pyrolysis alone or in combination with additional

-17-

processes, a wide variety of metal oxide particles can be produced.

Manganese oxide nanoparticles produced by laser pyrolysis are a preferred starting material for the lithium incorporation process described herein involving the mild heating of manganese oxide nanoparticles with a lithium compound. In addition, lithium manganese oxide nanoparticles can be produced directly by laser pyrolysis, where heating can be used to alter and/or improve the characteristics of the resulting particles. The lithium manganese oxide nanoparticles formed by laser pyrolysis can be either amorphous or crystalline.

The reaction conditions determine the qualities of the particles produced by laser pyrolysis. The reaction conditions for laser pyrolysis can be controlled relatively precisely in order to produce particles with desired properties. The appropriate reaction conditions to produce a certain type of particles generally depend on the design of the particular apparatus. Specific conditions used to produce manganese oxide particles in two particular apparatuses and lithium manganese oxide in the first particular apparatus with two different reactant delivery systems are described below in the Examples. Furthermore, some general observations on the relationship between reaction conditions and the resulting particles can be made.

Increasing the laser power results in increased reaction temperatures in the reaction region as well as a faster quenching rate. A rapid quenching rate tends to favor production of high energy phases, which may not be obtained with processes near thermal equilibrium. Similarly, increasing the chamber pressure

-18-

also tends to favor the production of higher energy structures. Also, increasing the concentration of the reactant serving as the oxygen source in the reactant stream favors the production of particles with increased amounts of oxygen.

Reactant flow rate and velocity of the reactant gas stream are inversely related to particle size so that increasing the reactant gas flow rate or velocity tends to result in smaller particle sizes. Also, the growth dynamics of the particles have a significant influence on the size of the resulting particles. In other words, different forms of a product compound have a tendency to form different size particles from other phases under relatively similar conditions. Laser power also influences particle size with increased laser power favoring larger particle formation for lower melting materials and smaller particle formation for higher melting materials.

Laser pyrolysis has been performed generally with gas phase reactants. The use of exclusively gas phase reactants is somewhat limiting with respect to the types of precursor compounds that can be used. Thus, techniques have been developed to introduce aerosols containing reactant precursors into laser pyrolysis chambers. The aerosol atomizers can be broadly classified as ultrasonic atomizers, which use an ultrasonic transducer to form the aerosol, or as mechanical atomizers, which use energy from one or more flowing fluids (liquids, gases, or supercritical fluids) themselves to form the aerosol. Improved aerosol delivery apparatuses for reactant systems are described further in commonly assigned and copending U.S. Patent Application Serial Number 09/188,670 to Gardner et al.,

-19-

entitled "Reactant Delivery Apparatuses," filed November 9, 1998, incorporated herein by reference.

Using aerosol delivery apparatuses, solid precursor compounds can be delivered by dissolving the 5 compounds in a solvent. Alternatively, powdered precursor compounds can be dispersed in a liquid\solvent for aerosol delivery. Liquid precursor compounds can be delivered as an aerosol from a neat liquid, a multiple liquid dispersion or a liquid solution, if desired. 10 Aerosol reactants can be used to obtain a significant reactant throughput. The solvent, if any, can be selected to achieve desired properties of the solution. Suitable solvents include water, methanol, ethanol, isopropyl alcohol, other organic solvents and mixtures 15 thereof. The solvent should have a desired level of purity such that the resulting particles have a desired purity level. For the production of composite metal oxide particles by laser pyrolysis, a plurality of metal compounds can be included in the solution. 20 Alternatively or additionally, metal precursors can be delivered into the reaction chamber in the vapor state in addition to the metal precursors delivered as an aerosol.

If aerosol precursors are formed with a 25 solvent present, the solvent is rapidly evaporated by the laser beam in the reaction chamber such that a gas phase reaction can take place. Thus, the fundamental features of the laser pyrolysis reaction is unchanged. However, the reaction conditions are affected by the 30 presence of the aerosol. Below, examples are described for the production of manganese oxide nanoparticles using gaseous reaction precursors and aerosol precursors using two different laser pyrolysis reaction chambers. The production of lithium manganese oxide nanoparticles

-20-

by laser pyrolysis in one of these reaction chambers using aerosol precursors is also described in the Examples. Thus, the parameters associated with aerosol reactant delivery can be explored based on the 5 description below.

A number of suitable solid, manganese precursor compounds can be delivered as an aerosol from solution. For example, manganese chloride ( $MnCl_2$ ) and hydrated manganese chloride ( $MnCl_2 \cdot H_2O$ ) are soluble in 10 water and alcohols, and manganese nitrate ( $Mn(NO_3)_2$ ) is soluble in water and certain organic solvents. Also, suitable lithium precursors for aerosol delivery from solution include, for example, lithium chloride ( $LiCl$ ), which is somewhat soluble in water, alcohol and some 15 other organic solvents, and lithium nitrate ( $LiNO_3$ ), which is somewhat soluble in water and alcohol. In addition, suitable vanadium precursors for aerosol delivery from solution include, for example,  $VOCl_2$ , which is soluble in absolute alcohol.

The compounds are dissolved in a solution preferably with a concentration greater than about 0.5 molar. Generally, the greater the concentration of precursor in the solution the greater the throughput of reactant through the reaction chamber. As the 25 concentration increases, however, the solution can become more viscous such that the aerosol has droplets with larger sizes than desired. Thus, selection of solution concentration can involve a balance of factors in the selection of a preferred solution concentration.

For the formation of composite metal particles, the relative amounts of metal precursors in the solution effects the relative amounts of metals in the resulting particles. Thus, the desired composition 30 of the product particles influences the selection of the

-21-

relative amounts of metal precursors for delivery. While a desired stoichiometry may influence the relative amounts of metals delivered into the reaction chamber, the relative amounts of metal precursors may alter the 5 portion of the phase diagram sampled such that a different material or mixed phase material can be produced. Since mixed phase materials may be produced, the relative amounts of metals in the reactant stream does not directly translate into particles with a 10 corresponding stoichiometry.

As noted above, the reaction conditions determine the type and characteristics of the particles produced by laser pyrolysis. Of course, with the production of composite metal oxide particles, the 15 situation is even more complicated because of the added complexity of the corresponding phase diagram. There is an additional parameter, namely, the quantity of additional metal precursor that effects the resulting properties of the particle(s). One can be guided by known stoichiometries of stable crystalline forms in the 20 selection of the relative amounts of metal precursors, although phase diagrams may not be known completely, and the non-equilibrium conditions in the laser pyrolysis apparatus may lead to additional uncertainty.

In the production of lithium manganese oxide 25 that the composition of the metal precursors influences the crystallinity of the resultant nanoparticles. In particular, metal chloride precursors favor the production of amorphous particles while metal nitrates favor the production of crystalline particles. Based on 30 kinetic principles, higher quench rates favor amorphous particle formation while slower quench rates favor crystalline particle formation. Faster quenches are

- 22 -

accomplished by a fasted reactant stream velocity through the reaction zone.

Appropriate manganese precursor compounds for gaseous delivery generally include manganese compounds with reasonable vapor pressures, i.e., vapor pressures sufficient to get desired amounts of precursor vapor in the reactant stream. The vessel holding liquid or solid precursor compounds can be heated to increase the vapor pressure of the manganese precursor, if desired. Suitable solid, manganese precursors with sufficient vapor pressure of gaseous delivery include, for example, manganese carbonyl ( $Mn_2(CO)_{10}$ ). A suitable container for heating and delivering a solid precursor to a laser pyrolysis apparatus is shown in Fig. 1.

Referring to Fig. 1, the solid precursor delivery system 50 for vapor delivery includes a container 52 and a lid 54. A gasket 56 is located between container 52 and lid 54. In one preferred embodiment, container 52 and lid 54 are made from stainless steel, and gasket 56 is made from copper. In this embodiment, lid 54 and gasket 56 are bolted to container 52. Other inert materials, such as Pyrex®, suitable for the temperatures and pressures applied to the solid precursor system can be used. Container 52 is surrounded with a band heater 58, which is used to set the temperature of the delivery system 50 at desired values. Suitable band heaters are available from Omega Engineering Inc. Stamford, Conn. The temperature of the band heater can be adjusted to yield a desired vapor pressure of the precursor compound. Additional portions of the precursor delivery system can be heated to maintain the precursor in a vapor state after it has left container 52.

-23-

Preferably, a thermocouple 60 is inserted into container 52 through lid 54. Thermocouple 60 can be inserted by way of a Swagelok® fitting 62 or other suitable connection. Tubing 64 provides a input flow of 5 a carrier gas into container 52. Tubing 64 preferably includes a shut off valve 66 and can be inserted through lid 54 by way of a Swagelok® fitting 68 or other suitable connection. Output tube 70 also preferably includes a shut off valve 72. Output tube 70 preferably 10 enters into container 52 through lid 54 at a sealed connection 74. Tubes 64 and 70 can be made of any suitable inert material such as stainless steel. A solid precursor can be placed directly within container 52 or it can be placed within a smaller, open container 15 within container 52.

Preferred secondary reactants serving as oxygen source include, for example, O<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>3</sub> and mixtures thereof. The secondary reactant compound should not react significantly with the manganese precursor and/or lithium precursor prior to entering the reaction zone since this generally would result in the formation of large particles.

Laser pyrolysis can be performed with a variety of optical frequencies. Preferred light sources 25 operate in the infrared portion of the electromagnetic spectrum. CO<sub>2</sub> lasers are particularly preferred sources of light. Infrared absorbers for inclusion in the molecular stream include, for example, C<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, SF<sub>6</sub>, SiH<sub>4</sub> and O<sub>3</sub>. O<sub>3</sub> can act as both an infrared absorber and 30 as an oxygen source. The radiation absorber, such as the infrared absorber, absorbs energy from the radiation beam and distributes the energy to the other reactants to drive the pyrolysis.

- 24 -

Preferably, the energy absorbed from the light beam increases the temperature at a tremendous rate, many times the rate that heat generally would be produced even by strongly exothermic reactions under controlled condition. While the process generally involves nonequilibrium conditions, the temperature can be described approximately based on the energy in the absorbing region. The laser pyrolysis process is qualitatively different from the process in a combustion reactor where an energy source initiates a reaction, but the reaction is driven by energy given off by an exothermic reaction. Laser pyrolysis requires continuous input of laser energy to sustain the chemical reaction.

An inert shielding gas can be used to reduce the amount of reactant and product molecules contacting the reactant chamber components. Appropriate shielding gases include, for example, Ar, He and N<sub>2</sub>.

An appropriate laser pyrolysis apparatus generally includes a reaction chamber isolated from the ambient environment. A reactant inlet connected to a reactant supply system produces a reactant stream through the reaction chamber. A laser beam path intersects the reactant stream at a reaction zone. The reactant stream continues after the reaction zone to an outlet, where the reactant stream exits the reaction chamber and passes into a collection system. Generally, the laser is located external to the reaction chamber, and the light beam enters the reaction chamber through an appropriate window.

Two laser pyrolysis reaction chambers are described further below. These laser pyrolysis reaction chambers can be configured for delivery of gas phase reactants and/or aerosol reactants.

-25-

1. First Laser Pyrolysis Reaction Chamber

Referring to Fig. 2, a particular embodiment 100 of a laser pyrolysis apparatus involves a reactant supply system 102, reaction chamber 104, collection system 106, laser 108 and shielding gas delivery system 110. Two alternative types of reaction supply systems can be used with the apparatus of Fig. 2. The first type of reaction supply system is used to deliver exclusively gaseous reactants. The second type of reactant supply system is used to deliver one or more reactants as an aerosol.

Referring to Fig. 3, a first embodiment 112 of reactant supply system 102 includes a source 120 of precursor compound. An optional second precursor source 121 can be used for the production of composite/ternary particles. For liquid or solid precursors, a carrier gas from one or more carrier gas sources 122 can be introduced into precursor source 120 and/or 121 to facilitate delivery of the precursor as a vapor. Precursor sources 120 and/or 121 can be a solid precursor delivery system 50, as shown in Fig. 1. The carrier gas from source 122 preferably is either an infrared absorber or an inert gas and is preferably bubbled through a liquid precursor compound or delivered into a solid precursor delivery system. Inert gas used as a carrier gas can moderate the reaction conditions. The quantity of precursor vapor in the reaction zone is roughly proportional to the flow rate of the carrier gas.

Alternatively, carrier gas can be supplied directly from infrared absorber source 124 or inert gas source 126, as appropriate. The secondary reactant can be supplied from reactant source 128, which can be a gas cylinder or other suitable container. The gases from

-26-

the precursor sources 120, 121 are mixed with gases from reactant source 128, infrared absorber source 124 and inert gas source 126 by combining the gases in a single portion of tubing 130. The gases are combined a sufficient distance from reaction chamber 104 such that the gases become well mixed prior to their entrance into reaction chamber 104.

The combined gas in tube 130 passes through a duct 132 into rectangular channel 134, which forms part of an injection nozzle for directing reactants into the reaction chamber. Portions of reactant supply system 112 can be heated to inhibit the deposition of precursor compound on the walls of the delivery system.

Referring to Fig. 4A, a second embodiment 150 of the reactant supply system 102 is used to supply an aerosol to duct 132. Duct 132 connects with rectangular channel 134, which forms part of an injection nozzle for directing reactants into the reaction chamber. Reactant supply system 150 includes a delivery tube 152 that is connected to duct 132. Venturi tube 154 connects to delivery tube 152 as a source of the aerosol. Venturi tube 154 is connected to gas supply tube 156 and liquid supply tube 158.

Gas supply tube 156 is connected to gas source 160. Gas source 160 can include a plurality of gas containers that are connected to deliver a selected gas or gas mixture to gas supply tube 156. The flow of gas from gas source 160 to gas supply tube 156 is controlled by one or more valves 162. Liquid supply tube 158 is connected to liquid supply 164. Delivery tube 152 also connects with drain 166 that flows to reservoir 168.

In operation, gas flow through venturi tube 154 creates suction that draws liquid into venturi tube 154 from liquid supply tube 158. The gas-liquid mixture

- 27 -

in venturi tube 154 forms an aerosol when venturi tube 154 opens into delivery tube 152. The aerosol is drawn up into duct 132 by pressure differentials within the system. Any aerosol that condenses within delivery tube 5 152 is collected in reservoir 168, which is part of the closed system.

Referring to Fig. 4B, a third embodiment 170 of the reactant supply system 102 can be used to supply an aerosol to duct 132. Reactant supply system 170 10 includes an aerosol generator 172, carrier gas/vapor supply tube 174 and junction 176. Duct 132, aerosol generator 172 and supply tube 174 meet within interior volume 178 of junction 176. Supply tube 174 is oriented to direct carrier gas along duct 132. Aerosol generator 15 172 is mounted such that an aerosol 180 is generated in the volume of chamber 178 between the opening into duct 132 and the outlet from supply tube 174.

Aerosol generator 172 can operate based on a variety of principles. For example, the aerosol can be 20 produced with an ultrasonic nozzle, with an electrostatic spray system, with a pressure-flow or simplex atomizer, with an effervescent atomizer or with a gas atomizer where liquid is forced under significant pressure through a small orifice and sheared into droplets by a colliding gas stream. Suitable ultrasonic nozzles can include piezoelectric transducers. Ultrasonic nozzles with piezoelectric transducers and suitable broadband ultrasonic generators are available 25 from Sono-Tek Corporation, Milton, NY, such as model 8700-120. Suitable aerosol generators are described further in copending and commonly assigned, U.S. Patent Application Serial No. 09/188,670 to Gardner et al., 30 entitled "REACTANT DELIVERY APPARATUSES," incorporated herein by reference. Additional aerosol generators can

-28-

be attached to junction 176 through other ports 182 such that additional aerosols can be generated in interior 178 for delivery into the reaction chamber.

Junction 176 includes ports 182 to provide  
5 access from outside junction 176 to interior 178. Thus,  
duct 132, aerosol generator 172 and supply tube 174 can  
be mounted appropriately. In one embodiment, junction  
176 is cubic with six cylindrical ports 182, with one  
port 182 extending from each face of junction 176.  
10 Junction 176 can be made from stainless steel or other  
durable, noncorrosive material. A window 181 preferably  
is sealed at one port 182 to provide for visual  
observation into interior 178. The port 182 extending  
from the bottom of junction 176 preferably includes a  
15 drain 183, such that condensed aerosol that is not  
delivered through duct 132 can be removed from junction  
176.

Carrier gas/vapor supply tube 174 is connected  
to gas source 184. Gas source 184 can include a  
20 plurality of gas containers, liquid reactant delivery  
apparatuses, and/or a solid reactant delivery  
apparatuses, which are connected to deliver a selected  
gas or gas mixture to supply tube 174. Thus, carrier  
gas/vapor supply tube 174 can be used to deliver a  
25 variety of desired gases and/or vapors within the  
reactant stream including, for example, laser absorbing  
gases, reactants, and/or inert gases. The flow of gas  
from gas source 184 to supply tube 174 preferably is  
controlled by one or more mass flow controllers 186.  
30 Liquid supply tube 188 is connected to aerosol generator  
152. Liquid supply tube 188 is connected to liquid  
supply 189.

For the production of lithium manganese oxide  
particles, liquid supply 189 can hold a liquid

-29-

comprising both a lithium precursor and a manganese precursor. Alternatively, for the production of lithium manganese oxide particles, liquid supply 189 can hold a liquid comprising manganese precursor while a lithium precursor is delivered by way of vapor supply tube 174 and gas source(s) 184. Similarly, if desired, liquid supply 189 can hold a liquid comprising lithium precursor, while a manganese precursor is delivered by way of vapor supply tube 174 and gas source(s) 184.

5      Also, two separate aerosol generators 172 can be used to generate aerosol within junction 176, with one producing 10     an aerosol with manganese precursor and the second producing aerosol with a lithium precursor.

In the embodiment shown in Fig. 4B, aerosol generator 172 generates an aerosol with momentum roughly orthogonal to the carrier gas flow from tube 174 to duct 132. Thus, carrier gas/vapor from supply tube 174 directs aerosol precursor generated by aerosol generator 172 into duct 132. In operation, carrier gas flow 20     directs the aerosol delivered within chamber 178 into duct 132. In this way, the delivery velocity of the aerosol is determined effectively by the flow rate of the carrier gas.

In alternative preferred embodiments, the aerosol generator is placed at an upward angle relative 25     to the horizontal, such that a component of the forward momentum of the aerosol is directed along duct 132. In a preferred embodiment, the output directed from the aerosol generator is placed at about a 45° angle 30     relative to the normal direction defined by the opening into duct 132, i.e. the direction of the flow into duct 132 from supply tube 174.

Referring to Fig. 4C, another embodiment 191 of the reactant supply system 102 can be used to supply

-30-

an aerosol to duct 132. Reactant supply system 191 includes an outer nozzle 193 and an inner nozzle 195. Outer nozzle 193 has an upper channel 197 that leads to a 5/8 in. by 1/4 in. rectangular outlet 199 at the top 5 of outer nozzle 193, as shown in the insert in Fig. 4C. Outer nozzle 193 includes a drain tube 201 in base plate 203. Drain tube 201 is used to remove condensed aerosol from outer nozzle 193. Inner nozzle 195 is secured to outer nozzle 193 at fitting 205.

10           Inner nozzle 195 is a gas atomizer from Spraying Systems (Wheaton, IL), such as model number 17310-12-1x8jj. The inner nozzle has about a 0.5 inch diameter and a 12.0 inch length. The top of the nozzle is a twin orifice internal mix atomizer 207 (0.055 in. 15 gas orifice and 0.005 in. liquid orifice). Liquid is fed to the atomizer through tube 209, and gases for introduction into the reaction chamber are fed to the atomizer through tube 211. Interaction of the gas with the liquid assists with droplet formation.

20           Outer nozzle 193 and inner nozzle 195 are assembled concentrically. Outer nozzle 193 shapes the aerosol generated by inner nozzle 195 such that it has a flat rectangular cross section. In addition, outer nozzle 193 helps to achieve a uniform aerosol velocity 25 and a uniform aerosol distribution along the cross section. Outer nozzle 193 can be reconfigured for different reaction chambers. The height of outer nozzle 193 relative to the radiation/laser beam can be adjusted to produce spray characteristics that result in desired 30 particle properties. For the production of lithium manganese oxide by laser pyrolysis, outer nozzle 193 is spaced about 3 inches below the laser beam.

Referring to Fig. 2, shielding gas delivery system 110 includes inert gas source 190 connected to an

-31-

inert gas duct 192. Inert gas duct 192 flows into annular channel 194. A mass flow controller 196 regulates the flow of inert gas into inert gas duct 192. If reactant delivery system 112 is used, inert gas source 126 can also function as the inert gas source for duct 192, if desired.

The reaction chamber 104 includes a main chamber 200. Reactant supply system 102 connects to the main chamber 200 at injection nozzle 202. Reaction chamber 104 can be heated to keep the precursor compound in the vapor state. The chamber preferably is heated to a surface temperature above the dew point of the mixture of reactants and inert components at the pressure in the apparatus. For many embodiments, the chamber is heated to about 120° when a solid precursor is used. Similarly, for many embodiments, the argon shielding gas is preferably heated to about 150°C when a solid precursor is used. The chamber can be examined for condensation to ensure that precursor is not deposited on the chamber.

The end of injection nozzle 202 has an annular opening 204 for the passage of inert shielding gas, and a reactant inlet 206 for the passage of reactants to form a reactant stream in the reaction chamber. Reactant inlet 206 preferably is a slit, as shown in the lower insert of Fig. 2. Annular opening 204 has, for example, a diameter of about 1.5 inches and a width along the radial direction from about 1/8 in to about 1/16 in. The flow of shielding gas through annular opening 204 helps to prevent the spread of the reactant gases and product particles throughout reaction chamber 104.

Tubular sections 208, 210 are located on either side of injection nozzle 202. Tubular sections

-32-

208, 210 include ZnSe windows 212, 214, respectively. Windows 212, 214 are about 1 inch in diameter. Windows 212, 214 are preferably cylindrical lenses with a focal length equal to the distance between the center of the 5 chamber to the surface of the lens to focus the light beam to a point just below the center of the nozzle opening. Windows 212, 214 preferably have an antireflective coating. Appropriate ZnSe lenses are available from Laser Power Optics, San Diego, California. Tubular sections 208, 210 provide for the displacement of windows 212, 214 away from main chamber 200 such that windows 212, 214 are less likely to be contaminated by reactants and/or products. Window 212, 214 are displaced, for example, about 3 cm from the edge 10 15 of the main chamber 200.

Windows 212, 214 are sealed with a rubber o-ring to tubular sections 208, 210 to prevent the flow of ambient air into reaction chamber 104. Tubular inlets 216, 218 provide for the flow of shielding gas into 20 tubular sections 208, 210 to reduce the contamination of windows 212, 214. Tubular inlets 216, 218 are connected to inert gas source 190 or to a separate inert gas source. In either case, flow to inlets 216, 218 preferably is controlled by a mass flow controller 220.

Light source 108 is aligned to generate a light beam 222 that enters window 212 and exits window 214. Windows 212, 214 define a light path through main chamber 200 intersecting the flow of reactants at reaction zone 224. After exiting window 214, light beam 222 strikes power meter 226, which also acts as a beam dump. An appropriate power meter is available from 25 30 Coherent Inc., Santa Clara, CA. Light source 108 can be a laser or an intense conventional light source such as an arc lamp. Preferably, light source 108 is an

-33-

infrared laser, especially a CW CO<sub>2</sub> laser such as an 1800 watt maximum power output laser available from PRC Corp., Landing, NJ.

Reactants passing through reactant inlet 206 in injection nozzle 202 initiate a reactant stream. The reactant stream passes through reaction zone 224, where reaction involving the metal precursor compounds takes place. Heating of the gases in reaction zone 224 is extremely rapid, roughly on the order of 10<sup>5</sup> degree C/sec depending on the specific conditions. The reaction is rapidly quenched upon leaving reaction zone 224, and particles 228 are formed in the reactant stream. The nonequilibrium nature of the process allows for the production of nanoparticles with a highly uniform size distribution and structural homogeneity.

The path of the reactant stream continues to collection nozzle 230. Collection nozzle 230 is spaced about 2 cm from injection nozzle 202. The small spacing between injection nozzle 202 and collection nozzle 230 helps reduce the contamination of reaction chamber 104 with reactants and products. Collection nozzle 230 has a circular opening 232, as shown in the upper insert of Fig. 2. Circular opening 232 feeds into collection system 106.

The chamber pressure is monitored with a pressure gauge attached to the main chamber. The preferred chamber pressure for the production of the desired oxides generally ranges from about 80 Torr to about 650 Torr.

Reaction chamber 104 has two additional tubular sections not shown. One of the additional tubular sections projects into the plane of the sectional view in Fig. 2, and the second additional tubular section projects out of the plane of the

-34-

sectional view in Fig. 2. When viewed from above, the four tubular sections are distributed roughly, symmetrically around the center of the chamber. These additional tubular sections have windows for observing 5 the inside of the chamber. In this configuration of the apparatus, the two additional tubular sections are not used to facilitate production of particles.

Collection system 106 preferably includes a curved channel 270 leading from collection nozzle 230. 10 Because of the small size of the particles, the product particles follow the flow of the gas around curves. Collection system 106 includes a filter 272 within the gas flow to collect the product particles. Due to curved section 270, the filter is not supported directly 15 above the chamber. A variety of materials such as Teflon, glass fibers and the like can be used for the filter as long as the material is inert and has a fine enough mesh to trap the particles. Preferred materials for the filter include, for example, a glass fiber 20 filter from ACE Glass Inc., Vineland, NJ and cylindrical Nomex® filters from AF Equipment Co., Sunnyvale, CA.

Pump 274 is used to maintain collection system 106 at a selected pressure. A variety of different pumps can be used. Appropriate pumps for use as pump 25 274 include, for example, Busch Model B0024 pump from Busch, Inc., Virginia Beach, VA with a pumping capacity of about 25 cubic feet per minute (cfm) and Leybold Model SV300 pump from Leybold Vacuum Products, Export, PA with a pumping capacity of about 195 cfm. It may be 30 desirable to flow the exhaust of the pump through a scrubber 276 to remove any remaining reactive chemicals before venting into the atmosphere. The entire apparatus 100 can be placed in a fume hood for ventilation purposes and for safety considerations.

-35-

Generally, the laser remains outside of the fume hood because of its large size.

The apparatus is controlled by a computer. Generally, the computer controls the light source and monitors the pressure in the reaction chamber. The computer can be used to control the flow of reactants and/or the shielding gas. The pumping rate is controlled by either a manual needle valve or an automatic throttle valve inserted between pump 274 and filter 272. As the chamber pressure increases due to the accumulation of particles on filter 272, the manual valve or the throttle valve can be adjusted to maintain the pumping rate and the corresponding chamber pressure.

The reaction can be continued until sufficient particles are collected on filter 272 such that pump 274 can no longer maintain the desired pressure in the reaction chamber 104 against the resistance through filter 272. When the pressure in reaction chamber 104 can no longer be maintained at the desired value, the reaction is stopped, and filter 272 is removed. With this embodiment, about 1-300 grams of particles can be collected in a single run before the chamber pressure can no longer be maintained. A single run generally can last up to about 10 hours depending on the reactant delivery system, the type of particle being produced and the type of filter being used.

The reaction conditions can be controlled relatively precisely. In particular, the mass flow controllers are quite accurate. The laser generally has about 0.5 percent power stability. With either a manual control or a throttle valve, the chamber pressure can be controlled to within about 1 percent.

The configuration of the reactant supply system 102 and the collection system 106 can be

-36-

reversed. In this alternative configuration, the reactants are supplied from the top of the reaction chamber, and the product particles are collected from the bottom of the chamber. In the alternative 5 configuration, the collection system may not include a curved section so that the collection filter is mounted directly below the reaction chamber.

2. Second Laser Pyrolysis Reaction Chamber

An alternative design of a laser pyrolysis apparatus has been described in U.S. Patent 5,958,348, 10 entitled "Efficient Production of Particles by Chemical Reaction," incorporated herein by reference. This alternative design is intended to facilitate production of commercial quantities of particles by laser pyrolysis. The reaction chamber is elongated along the 15 light beam in a dimension perpendicular to the reactant stream to provide for an increase in the throughput of reactants and products. The original design of the apparatus was based on the introduction of purely 20 gaseous reactants. A particular embodiment for the introduction of an aerosol into the apparatus is described below. Additional embodiments for the introduction of an aerosol with one or more aerosol generators into an elongated reaction chamber is 25 described in commonly assigned and copending U.S. Patent application serial No. 09/188,670 to Gardner et al., entitled "Reactant Delivery Apparatuses," filed November 9, 1998, incorporated herein by reference.

In general, the alternative pyrolysis apparatus includes a reaction chamber designed to reduce 30 contamination of the chamber walls, to increase the production capacity and to make efficient use of resources. To accomplish these objectives, an elongated reaction chamber is used that provides for an increased

-37-

throughput of reactants and products without a corresponding increase in the dead volume of the chamber. The dead volume of the chamber can become contaminated with unreacted compounds and/or reaction  
5 products.

The design of the improved reaction chamber 300 is shown schematically in Fig. 5. A reactant inlet 302 leads to main chamber 304. Reactant inlet 302 conforms generally to the shape of main chamber 304.  
10 The introduction of reactants through reactant inlet 302, for example, for the production of lithium manganese oxide particles can be performed by adapting the discussion above regarding the introduction of aerosol and/or vapor precursors with the laser pyrolysis  
15 apparatus of Fig. 1, appropriately adapted for the alternative structure of the reactant inlet. Generally, the reactant inlet has a length from about 5 mm to about 1 meter when used with an 1800 watt CO<sub>2</sub> laser.

Main chamber 304 includes an outlet 306 along  
20 the reactant/product stream for removal of particulate products, any unreacted gases and inert gases. Shielding gas inlets 310 are located on both sides of reactant inlet 302. Shielding gas inlets are used to form a blanket of inert gases on the sides of the  
25 reactant stream to inhibit contact between the chamber walls and the reactants or products.

Tubular sections 320, 322 extend from the main chamber 304. Tubular sections 320, 322 hold windows 324, 326 to define a light beam path 328 through the  
30 reaction chamber 300. Tubular sections 320, 322 can include inert gas inlets 330, 332 for the introduction of inert gas into tubular sections 320, 322.

Referring to Figs. 6-8, a specific embodiment  
350 of a laser pyrolysis reaction system with an

-38-

elongated reaction chamber is shown. In this embodiment, an aerosol reactant delivery apparatus is adapted for use with the elongated reaction chamber. Laser pyrolysis reaction system 350 includes reaction 5 chamber 352, a particle collection system 354, laser 356 and a reactant delivery system (described below). Reaction chamber 352 includes reactant inlet 364 at the bottom of reaction chamber 352 where the reactant delivery system connects with reaction chamber 352. In 10 this embodiment, the reactants are delivered from the bottom of the reaction chamber while the products are collected from the top of the reaction chamber. The configuration can be reversed with the reactants supplied from the top and product collected from the 15 bottom, if desired.

Shielding gas conduits 365 are located on the front and back of reactant inlet 364. Inert gas is delivered to shielding gas conduits 365 through ports 367. The shielding gas conduits direct shielding gas 20 along the walls of reaction chamber 352 to inhibit association of reactant gases or products with the walls.

Reaction chamber 352 is elongated along one dimension denoted in Fig. 6 by "w". A laser beam path 25 366 enters the reaction chamber through a window 368 displaced along a tube 370 from main chamber 372 and traverses the elongated direction of reaction chamber 352. The laser beam passes through tube 374 and exits window 376. In one preferred embodiment, tubes 370 and 30 374 displace windows 368 and 376 about 11 inches from main chamber 372. The laser beam terminates at beam dump 378. In operation, the laser beam intersects a reactant stream generated through reactant inlet 364.

-39-

The top of main chamber 372 opens into particle collection system 354. Particle collection system 354 includes outlet duct 380 connected to the top of main chamber 372 to receive the flow from main 5 chamber 372. Outlet duct 380 carries the product particles out of the plane of the reactant stream to a cylindrical filter 382. Filter 382 has a cap 384 on one end. The other end of filter 382 is fastened to disc 386. Vent 388 is secured to the center of disc 386 to 10 provide access to the center of filter 382. Vent 388 is attached by way of ducts to a pump. Thus, product particles are trapped on filter 382 by the flow from the reaction chamber 352 to the pump. Suitable pumps were described above with respect to the first laser 15 pyrolysis apparatus in Fig. 2. Suitable filters for use as filter 382 include, for example, an air cleaner filter for a Saab 9000 automobile (Purilator part A44-67), which is wax impregnated paper with Plasticol or polyurethane end cap 384.

20 Referring to Fig. 9, an aerosol delivery apparatus 480 includes an aerosol generator 482, which is supported by mount 484 and a cap 486. Aerosol delivery apparatus 480 is secured to reactant inlet 364 of reaction chamber 352 to extend within main chamber 25 372, shown in Figs. 6-8. Mount 484 is connected to a base plate 488. Base plate 488 is fastened to reactant inlet 364 with bolts 490. An o-ring or the like, suitably shaped, can be placed within hollow 492 to form a seal between base plate 488 and reactant inlet 364.

30 Referring to Figs. 10 and 11, mount 484 has a generally cylindrical shape. Mount 484 includes a lip 506 extending within cylindrical cavity 508. Lip 506 helps support aerosol generator 482. In this embodiment, lip 506 includes a notch 510, which allows

-40-

a portion of aerosol generator 482 to extend past lip 506. Top surface 512 of mount 484 includes a hollow 514 for holding an o-ring or the like to form a seal with cap 486 or a spacer, described below. Mount 484 further 5 includes threads 518 on the outer surface 520.

Referring to Figs. 10, 12 and 13, cap 486 attaches over the top of mount 484. Cap 486 includes threads 528 that are mated with threads 518 on mount 484. Flange 530 can be used to form a seal with an o-ring or the like. Surface 532 includes hollow 534. Hollow 534 can hold an o-ring or the like to form a seal with aerosol generator 482 or a shim, described further below.

Tube 536 is in fluid communication with cavity 538. Tube 536 provides for gas flow into cavity 538. Cavity 538 vents through port 540. Tubes 542 provide for fluid flow through channels 544 into projecting tubes 546. In this embodiment, four projecting tubes 546 project toward the flow stream coming from aerosol generator 482 and port 540. Four projecting tubes 546 are symmetrically distributed around port 540. More or less than four projecting tubes 546 can be used, if desired. Gas can be supplied to tubes 536 and 542 through one or more ports 547 through base plate 488 (Fig. 9) by way of stainless steel tubing or the like.

The use of projecting tubes 546 are particularly useful to mix reactants further within the reaction chamber away from aerosol generator 482. Using projecting tubes 546, gases such as reactant gases and/or radiation absorbing gases can be mixed within reaction chamber 352 with reactants from aerosol generator 482 and/or port 540. Laser beam path 548 intersects the reaction stream just above projecting tubes 546.

-41-

The position of aerosol generator 482 relative to port 540 can affect the properties of the resulting reactant stream and thereby the properties of the reaction product. With an ultrasonic aerosol generator, 5 the tip of the aerosol generator preferably is located between positions just slightly below the cap surface to just slightly above the cap surface.

Spacer 550, shown in Fig. 14, can be placed between cap 486 and mount 484 to change the position of 10 aerosol generator 482 relative to port 540. Spacer 550 is a cylindrical piece with a hollow 552 along top surface 554 for holding an o-ring or the like. Top surface 554 seals against flange 530 of cap 486. Lower surface 556 of spacer 550 seals against top surface 512 of mount 484. A shim 558, as shown in Fig. 15, is 15 correspondingly placed between cap 486 and aerosol generator 482. Top surface 560 of shim 558 engages the o-ring in hollow 534. Flange 562 engages the aerosol generator 482.

20 The flow of reactants into main chamber 372 can be affected by the placement of a cap bushing at the opening of port 540. More specifically, a cap bushing can help provide a more confined reactant stream within main chamber 372. Three embodiments of cap bushings 25 570, 572, 574 are shown in Figs. 16-18, respectively. Referring to Fig. 16, cap bushing 570 has a cylindrical passage 576 and a flat upper surface 578 generally perpendicular to the central axis of cylindrical passage 576. Referring to Fig. 17, cap bushing 572 has a 30 conical passage 580 and a flat upper surface 582 generally perpendicular to the symmetry axis of conical passage 580. Referring to Fig. 18, cap bushing 574 has a conical passage 584 and a top surface with a flat section 586 and a conical section 588. Preferred

-42-

embodiments of cap bushings have a sharp edge between the internal passage and the top surface.

Reaction chamber 352 and reactant supply system 480 preferably are constructed from stainless steel or other corrosion resistant metal. O-rings and other seals can be made from natural or synthetic rubber or other polymers.

Referring to Fig. 10, in a preferred embodiment, aerosol generator 482 includes an ultrasonic nozzle 600 and nozzle supply 602. Preferred ultrasonic nozzle 600 is a model 8700-120 from Sono-Tek Corporation, Milton, NY. Referring to Figs. 19-20, ultrasonic nozzle 600 includes a nozzle tip 604, a nozzle body 606, a connector 608 for connection to an ultrasonic generator, and a liquid connection 610 for connection to a liquid reservoir directly or by way of nozzle supply 602. The end of nozzle tip 604 is an atomization surface 612. The size and shape of atomization surface 612 can be varied to yield a desirable spacial distribution of aerosol particles.

Nozzle tip 604 is connected to nozzle body 606 at or near top surface 614. Ultrasonic transducer 616 is located within nozzle body 606 at a suitable position to vibrate nozzle tip 604. Generally, ultrasonic transducer 616 is located toward top surface 614. Preferred ultrasonic transducers include, for example, piezoelectric transducers. Preferably, ultrasonic transducer 616 includes two or more piezoelectric transducers 618 coupled to oscillate in phase such that the amplitudes of the two vibrating piezoelectric transducers add to create an additive force at atomizing surface 612.

Ultrasonic transducer 616 is connected to an ultrasonic generator by way of connector 608. The

- 43 -

ultrasonic generator preferably is a broad band generator operating over a frequency range from about 20 kHz to about 120 kHz. The electrical signal from the ultrasonic generator is conveyed from connector 608 to 5 ultrasonic transducer 616 by way of conductors 620.

Liquid flows from liquid connection 610 to atomization surface 612 through channel 622, which runs through nozzle body 606. Referring to Fig. 10, nozzle supply 602 is connected to liquid connection 610 with a 10 liquid fitting 630. Nozzle supply 602 includes a needle valve with pneumatic control. Nozzle supply 602 has a pneumatic control inlet 632, a needle valve adjustment 634 and a liquid feedstock inlet 636. Pneumatic control inlet 632 and liquid feedstock inlet 636 are accessed 15 through central channel 508, which extends through base plate 488.

Liquid feedstock inlet 636 is connected to a liquid supply apparatus 640, shown schematically in Fig. 21. Liquid supply apparatus 640 includes, at least, one 20 liquid source 642, an outlet tube 644 and a gas supply tube 646. Tube 644 connects with fitting 648 to liquid feedstock inlet 636. Similarly, tube 644 is connected directly or indirectly to liquid source 642. Liquid 25 source 642 also connects to gas supply tube 646. Gas supply tube connects to a gas source 666, which can be a gas cylinder or the like. Flow from gas source 666 to gas supply tube 646 is controlled by one or more valves 668. Gas under pressure from gas supply tube 646 forces liquid from liquid source 642 into tube 644.

Proper placement of liquid source 642 can 30 result in gravity supplying the pressure as an alternative to using gas pressure. In other embodiments, mechanical pumps are used to supply a relatively constant amount of pressure within tube 644.

-44-

Suitable pumps include, for example, centrifical pumps and a plurality of syringe pumps that operate sequentially.

In use, the aerosol generator 482 produces an aerosol of a liquid supplied to aerosol generator 482. Aerosol generator 482 can deliver a gas along with the aerosol. Also, the aerosol can be combined with a gas supplied through tube 536. Thus, the aerosol and any gases supplied from aerosol generator 482 and/or tube 536 are directed into reaction chamber 352 near port 540 of cap 486. The aerosol and any gases emanating from aerosol generator 482 and/or tube 536 can be combined further within reaction chamber 352 with additional gases from projecting tubes 546. The resulting mixture of aerosol and gases is subsequently reacted within reaction chamber 352.

For the performance of laser pyrolysis based reaction synthesis, the aerosol/gas mixture generally includes one or more reactants in aerosol form, optionally, one or more additional reactant gases, a laser absorbing gas if the reactants and/or solvent(s) do not sufficiently absorb the laser radiation, and, optionally, an inert gas. The gases can be supplied from a pressurized cylinder or other suitable container. Multiple reactants can be mixed in the liquid phase and delivered as the aerosol.

Alternative aerosol generators can be used with the elongated reaction chamber. In addition, one or more aerosol generators can be configured with the elongated reaction chamber in a variety of ways.

B. Heat Processing

1. Particle Conditioning

As noted above, properties of the metal oxide particles can be modified by further processing.

-45-

Suitable starting material for the heat treatment include metal oxide particles, such as, lithium manganese oxide particles, produced by laser pyrolysis. In addition, particles used as starting material can 5 have been subjected to one or more prior heating steps under different conditions. For the heat processing of metal oxide particles formed by laser pyrolysis, the additional heat processing can improve the crystallinity, remove contaminants, such as elemental 10 carbon, and possibly alter the stoichiometry, for example, by incorporation of additional oxygen or of atoms from other gaseous species. The use of sufficiently mild conditions, i.e., temperatures well below the melting point of the particles, results in the 15 processing of the particles without significantly sintering the particles into larger particles.

The starting materials generally can be particles of any size and shape, although nanoscale particles are preferred starting materials. The 20 nanoscale particles have an average diameter of less than about 1000 nm and preferably from about 5 nm to about 500 nm, and more preferably from about 5 nm to about 150 nm. Suitable nanoscale starting materials have been produced by laser pyrolysis.

25 The metal oxide particles are preferably heated in an oven or the like to provide generally uniform heating. The processing conditions generally are mild, such that significant amounts of particle sintering does not occur. The temperature of heating preferably is low relative to the melting point of both the starting material and the product material.

For certain target product particles, additional heating does not lead to further variation in the particle composition once equilibrium has been

-46-

reached. The atmosphere for the heating process can be an oxidizing atmosphere or an inert atmosphere. In particular, for conversion of amorphous particles to crystalline particles or from one crystalline structure 5 to a different crystalline structure of essentially the same stoichiometry, the atmosphere generally can be inert. The atmosphere over the particles can be static, or gases can be flowed through the system.

Appropriate oxidizing gases include, for 10 example, O<sub>2</sub>, O<sub>3</sub>, CO, CO<sub>2</sub>, and combinations thereof. The O<sub>2</sub> can be supplied as air. Oxidizing gases optionally can be mixed with inert gases such as Ar, He and N<sub>2</sub>. When inert gas is mixed with the oxidizing gas, the gas mixture can include from about 1 percent oxidizing gas 15 to about 99 percent oxidizing gas, and more preferably from about 5 percent oxidizing gas to about 99 percent oxidizing gas. Alternatively, either essentially pure oxidizing gas or pure inert gas can be used, as desired.

The precise conditions can be altered to vary 20 the type of metal oxide particles that are produced. For example, the temperature, time of heating, heating and cooling rates, the gases and the exposure conditions with respect to the gases can all be changed, as desired. Generally, while heating under an oxidizing 25 atmosphere, the longer the heating period the more oxygen that is incorporated into the material, prior to reaching equilibrium. Once equilibrium conditions are reached, the overall conditions determine the crystalline phase of the powders.

A variety of ovens or the like can be used to 30 perform the heating. An example of an apparatus 660 to perform this processing is displayed in Fig. 22A. Apparatus 660 includes a jar 662, which can be made from glass or other inert material, into which the particles

-47-

are placed. Suitable glass reactor jars are available from Ace Glass (Vineland, NJ). The top of glass jar 662 is sealed to a glass cap 664, with a Teflon® gasket 666 between jar 662 and cap 664. Cap 664 can be held in place with one or more clamps. Cap 664 includes a plurality of ports 668, each with a Teflon® bushing. A multiblade stainless steel stirrer 670 preferably is inserted through a central port 668 in cap 664. Stirrer 670 is connected to a suitable motor.

One or more tubes 672 are inserted through ports 668 for the delivery of gases into jar 662. Tubes 672 can be made from stainless steel or other inert material. Diffusers 674 can be included at the tips of tubes 672 to disburse the gas within jar 662. A heater/furnace 676 generally is placed around jar 662. Suitable resistance heaters are available from Glas-col (Terre Haute, IN). One port preferably includes a T-connection 678. The temperature within jar 662 can be measured with a thermocouple 678 inserted through T-connection 678. T-connection 678 can be further connected to a vent 680. Vent 680 provides for the venting of gas circulated through jar 662. Preferably vent 680 is vented to a fume hood or alternative ventilation equipment.

Preferably, desired gases are flowed through jar 662. Tubes 672 generally are connected to an oxidizing gas source and/or an inert gas source. Oxidizing gas, inert gas or a combination thereof to produce the desired atmosphere are placed within jar 662 from the appropriate gas source(s). Various flow rates can be used. The flow rate preferably is between about 1 standard cubic centimeters per minute (sccm) to about 1000 sccm and more preferably from about 10 sccm to about 500 sccm. The flow rate generally is constant

-48-

through the processing step, although the flow rate and the composition of the gas can be varied systematically over time during processing, if desired. Alternatively, a static gas atmosphere can be used.

5       For the processing of manganese oxide and lithium manganese oxide nanoparticles, for example, the temperatures preferably range from about 50°C to about 600°C and more preferably from about 50°C to about 550°C, and even more preferably from about 60°C to about 10      400°C. The heating preferably is continued for greater than about 5 minutes, and generally is continued for from about 2 hours to about 120 hours, preferably from about 2 hours to about 25 hours. Some empirical adjustment may be required to produce the conditions 15      appropriate for yielding a desired material. The use of mild conditions avoids interparticle sintering resulting in larger particle sizes. Some controlled sintering of the particles can be performed at somewhat higher 20      temperatures to produce slightly larger, average particle diameters.

The conditions to convert crystalline VO<sub>2</sub> to orthorhombic V<sub>2</sub>O<sub>5</sub> and 2-D crystalline V<sub>2</sub>O<sub>5</sub>, and amorphous V<sub>2</sub>O<sub>5</sub> to orthorhombic V<sub>2</sub>O<sub>5</sub> and 2-D crystalline V<sub>2</sub>O<sub>5</sub> are described in copending and commonly assigned U.S. Patent 25      application serial number 08/897,903, to Bi et al., entitled "Processing of Vanadium Oxide Particles With Heat," incorporated herein by reference.

2.       Thermal Production of Lithium Manganese Oxide  
In an alternative approach to the formation of 30      lithium manganese oxide nanoparticles, it has been discovered that heat processing can be used to form nanoscale lithium manganese oxides. In a preferred approach to the thermal formation of lithium manganese oxide, manganese oxide nanoscale particles first are

-49-

mixed with a lithium compound. The resulting mixture is heated in an oven to form a lithium manganese oxide. The heating resulting in lithium incorporation into the manganese oxide lattice can be performed in an oxidizing environment or an inert environment. In either type of environment, the heating step generally results in alteration of the oxygen-to-manganese ratio, lithium-to-manganese ratio, lithium-to-oxygen ratio or a combination thereof.

The use of sufficiently mild conditions, i.e., temperatures well below the melting point of the manganese oxide particles, results in lithium incorporation into the manganese oxide particles without significantly sintering the particles into larger particles. The manganese oxide particles used for the lithiation process preferably are nanoscale manganese oxide particles. It has been discovered that spinel lithium manganese oxides can be formed from manganese oxides with an oxidation state less than +4. In particular, manganese oxides with an oxidation states from +2 ( $MnO$ ) to +4 ( $MnO_2$ ) can be used to form lithium manganese oxide spinels. Suitable manganese oxide nanoparticles can have a stoichiometry of, for example,  $MnO$ ,  $Mn_3O_4$ ,  $Mn_2O_3$ ,  $Mn_5O_8$ ,  $MnO_2$ , and corresponding mixed phase materials.

Suitable lithium compounds include for example, lithium nitrate ( $LiNO_3$ ), lithium chloride ( $LiCl$ ),  $Li_2CO_3$ ,  $LiOH$ ,  $LiOH \cdot H_2O$ ,  $Li_2C_2O_4$ ,  $LiHC_2O_4$ ,  $LiHC_2O_4 \cdot H_2O$ ,  $Li_3C_6H_5O_7 \cdot 4H_2O$ ,  $LiCOOH \cdot H_2O$ , and  $LiC_2H_3O_2 \cdot H_2O$ . Lithium incorporation into manganese oxide nanoparticles with some of these lithium compounds may require oxygen in the atmosphere during the heat processing. Appropriate oxidizing gases include, for example,  $O_2$ ,  $O_3$ ,  $CO$ ,  $CO_2$  and combinations thereof. The reactant gas

-50-

can be diluted with inert gases such as Ar, He and N<sub>2</sub>. For example, air and/or clean, dry air can be used as a source of oxygen and inert gas. Alternatively, the gas atmosphere can be exclusively inert gas. Lithium  
5 manganese oxides have been produced with either an inert atmosphere or an oxidizing atmosphere, as described in the Examples below.

In addition, the heat processing can result in an alteration of the crystal lattice and/or removal of  
10 adsorbed compounds on the particles to improve the quality of the particles. The processing generally of metal oxide nanoscale particles in an oven is discussed further in copending and commonly assigned, U.S. Patent Application Ser. No. 08/897,903, filed July 21, 1997,  
15 entitled "Processing of Vanadium Oxide Particles With Heat," incorporated herein by reference. In particular, heat processing under mild conditions can be used to alter the crystal structure of lithium manganese oxide nanoparticles formed by laser pyrolysis. Specifically,  
20 amorphous lithium manganese oxide can be annealed to crystalline, cubic spinel, lithium manganese oxide without sintering the particles into larger particles.

A variety of apparatuses can be used to perform the heat processing for lithium incorporation and/or annealing of a sample. For example, the heating apparatus shown in Fig. 22A, as described above, can be used to perform heat processing for lithium incorporation. Another embodiment of an apparatus 700 to perform this processing is displayed in Fig. 22B.  
25 Apparatus 700 includes a tube 702 into which the particles are placed. Tube 702 is connected to a reactant gas source 704 and inert gas source 706. Reactant gas, inert gas or a combination thereof are  
30

-51-

placed within tube 702 to produce the desired atmosphere.

Preferably, the desired gases are flowed through tube 702. Tube 702 is located within oven or furnace 708. Oven 708 maintains the relevant portions of the tube at a relatively constant temperature, although the temperature can be varied systematically through the processing step, if desired. Temperature in oven 708 generally is measured with a thermocouple 710. Vial 712 prevents loss of the particles due to gas flow. Vial 712 generally is oriented with the open end directed toward the direction of the source of the gas flow. To form lithium manganese oxide in the heating step, a mixture of manganese oxide particles and particles of lithium compound can be placed in tube 702 within a vial 712. In alternatively embodiments, lithium manganese oxide particles produced by laser pyrolysis are placed into vial 712 for heating in tube 702.

The precise conditions including type of oxidizing gas (if any), concentration of oxidizing gas, pressure or flow rate of gas, temperature and processing time can be selected to produce the desired type of product material. The temperatures generally are mild, i.e., significantly below the melting point of the material. The use of mild conditions avoids interparticle sintering resulting in larger particle sizes. Some controlled sintering of the particles can be performed in oven 708 at somewhat higher temperatures to produce slightly larger, average particle diameters.

For lithium incorporation into manganese oxide, the temperature preferably ranges from about 60°C to about 600°C and more preferably from about 100°C to about 550°C. The particles preferably are heated for